Precipitation of Ge nanoparticles from GeO_2 glasses in transmission electron microscope

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We show, using spatially resolved energy loss spectroscopy in a transmission electron microscopy (TEM), that GeO_2 and GeO_2-SiO_2 glasses are extremely sensitive to high energy electrons. Ge nanoparticles can be precipitated in GeO_2 glasses efficiently by the high-energy electron beam of a TEM. This is relevant to TEM characterization of luminescent Ge nanoparticles in silicate glasses, which may produce artificial results. © *2005 American Institute of Physics*.
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A Ge nanoparticle embedded into a dielectric matrix has attracted much attention due to its intense photoluminescence. Various methods have been claimed to be able to fabricate Ge nanoparticles, usually in amorphous SiO_2. The most popular method involves depositing GeO_2-SiO_2 on substrates (usually Si and SiO_2), either by cosputtering GeO_2 and SiO_2 or by oxidizing epitaxial $Si_{1-x}Ge_x$ films, following by postannealing processes. However, there is controversy over the postannealing treatments. Some studies reported that annealing environment must include reduction agent such as H_2, while the inactive agent such as N_2 plays no known role.[1–3] On the contrary, other studies claimed that Ge nanoparticles can be obtained by isothermal annealing in N_2 gas ambient,[4] and even in an Ar atmosphere.[5,6] Although the diffusion of Si from the substrates may provide reductant to reducing Ge from GeO_2,[5] some experiments were using fused quartz (amorphous SiO_2) rather than Si as substrates.[4,6]

In most of the publications related to this subject, the direct and important evidences of existing Ge nanoparticles in annealed samples were from (bright, dark-field, or phase contrast) images of transmission electron microscopy (TEM). However, none of these papers have ever mentioned whether high-energy (>100 keV) electron irradiation induced modifications in their observations. Extreme caution should be excised when materials which are extremely sensitive to electron irradiation, such as GeO_2-SiO_2, are observed using TEM. In our previous studies in a $10GeO_2-90SiO_2$ glass using scanning transmission electron microscopy (STEM), phase separation into Ge rich and poor regions was immediately observed once the sample was exposed to electrons under the normal operation conditions.[7] The electron beam current was 0.3 nA in a probe of diameter of 0.2 nm. In bright- and dark-field images, the appearances of the separated Ge-rich phases resemble the "nanoparticles" with an averaged size of 4 nm. Taking advantage of the subnanometer electron probe in STEM, we can also create nanorings and nanowires in the same samples.[8] The production of these nanofeatures is impressively efficient; only several tens of milliseconds are needed to create one structure. Even in amorphous SiO_2, the Si can also be reduced by electron irradiation in STEM (with a beam current of 1 nA in a probe of 15 nm in diameter), although several seconds of exposure are needed.[9] Although the illumination modes are different, the principles of STEM and TEM are the same. The electron-beam sensitivity of GeO_2-SiO_2 glasses is their nature. In order to re-emphasize the importance of irradiation modifications, we carried out *in situ* observations of GeO_2 glass in a conventional TEM. Here we report our results of the formation of Ge nanoparticles in GeO_2 glass only by electron irradiation. Most importantly, this work demonstrates how efficient it is to create such particles by high-energy electrons.

A sample used in this work is GeO_2 glass doped with 1 mol % Bi_2O_3. A glass sample was prepared by the conventional melting-quenching technique. 5N GeO_2 and 2N Bi_2O_3 were selected as the raw materials and a 20 g batch with the glass composition was mixed homogeneously in an agate mortar and then melted at 1550 °C in a platinum crucible for 20 min in air. The melt was cast and splashed onto a stainless-steel plate. The glass sample thus obtained was transparent and bubble free. The TEM specimens were prepared by picking up small pieces of crushed glass suspended in acetone using a lacy carbon film covered copper grid. Prior to loading into a microscope, the plasma clean was carried out in order to further remove the surface contamination. The specimen was then observed and analyzed in a JOEL 2010F (scanning) transmission electron microscope operating at 200 keV in TEM mode. The microscope is equipped with an electron source of a Shottky field emission gun, and a parallel-detection electron-energy-loss spectrometer. The energy resolution of the electron energy-loss spectra (EELS) was about 0.9 eV. The acquisition time for each spectrum is 0.2 s, and the recording time for each image is 1 s. The spectra have been deconvoluted from the plural scattering using Fourier-log method.[10]

Formation of nanoparticles in GeO_2 glass by electron irradiation can be observed by a series of time-resolved im-

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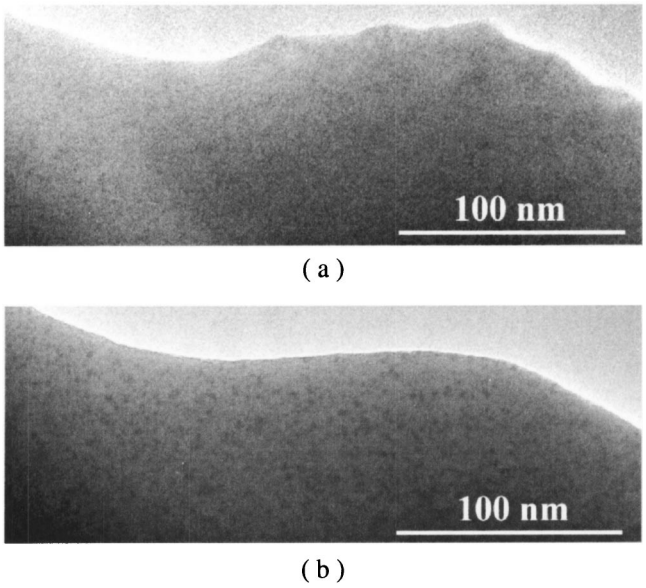

FIG. 1. TEM bright-field image showing formation of Ge nanoparticles in GeO_2 glass. (a) The first image of a series of time-resolved images. (b) The image after 1 min of irradiation. Both images are from the same area.

ages. In order to start from a "damage-free" image, illumination conditions, such as focusing, were set up in a nearby region prior to recording the series of images. The first image of the series is given in Fig. 1(a), in which there are no visible nanoparticle-like contrasts. The original shapes of crushed sample (rough edge) still remain. After 1 min of irradiation [Fig. 1(b)], however, nanoparticle-like contrasts (dark spots) appear. The size of these particles is about 3–4 nm in diameter. It is also noted that the edge becomes smooth in Fig. 1(b). The particles in Fig. 1(b) are not crystalline. The diffraction pattern from the area after 1 min of irradiation is still in amorphous form. However, the diffraction spots do appear in the patterns after several minutes of irradiation.

The process of formation of nanoparticles from GeO_2 glass can be monitored by *in situ* EELS. Similar to recording damage-free images, the electron beam was immediately moved to a fresh area after setting up illumination conditions on a nearby region, and started to acquire EELS spectra. The area of illumination is approximately 300 nm in diameter. The selected EELS spectra from a time series are shown in Fig. 2. It is seen that the fine structures of EELS change significantly with the increase of electron irradiation. In the initial spectrum (the first in the time series), the major peak at about 21.8 eV is the bulk plasmon of the GeO_2 glass. Its intensity decreases with the increase of irradiation. Meanwhile, a new peak appears at about 16.7 eV after 1 min of irradiation. This new peak is the bulk plasmon of Ge.[11] After 3 min, the bulk plasmon of GeO_2 is barely seen; instead the bulk plasmon of Ge becomes dominant.

The interpretation of a small peak at about 8 eV is not simple. In a crystalline (tetragonal) GeO_2, we have also observed the similar small peak at about 8 eV. This peak is believed to be an exciton of GeO_2, which is similar to the exciton at about 10 eV in SiO_2.[12] However, the relative intensity of this small peak increases with the decrease of intensity of bulk plasmon of GeO_2. We noted that the surface plasmon of Ge is about 11.0 eV,[13] and it is about 10 eV in Ge nanocrystal films.[14] It is also known that the surface plasmon excitation energy depends on the size of the nanoparticle, and they have a nonmonotonic relationship.[15] Averaging over a large variety of nanoparticles, a broad surface plasmon peak can be expected. Therefore, the interpretation of the evolution of small peak below 10 eV in our observations is suggested as follows. In the initial spectrum in Fig. 2, the peak below 10 eV is the exciton of GeO_2 glass. The intensity of the exciton peak gradually decreases, accompanying with the increase of the surface plasmon intensity of Ge, with the increase of electron irradiation. In the last spectrum in Fig. 2, it becomes dominant by the surface plasmon of Ge.

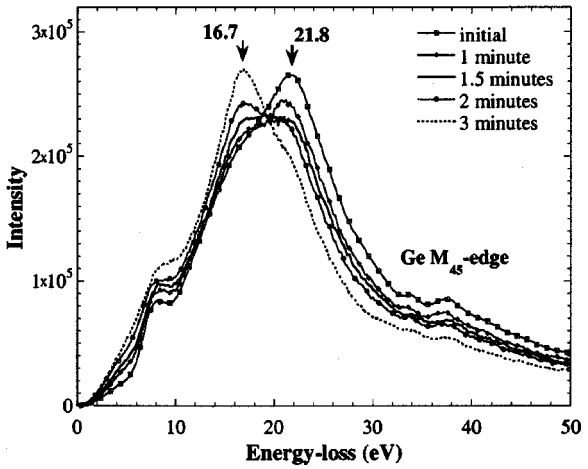

FIG. 2. Time-resolved EELS spectrum showing the evolution from GeO_2 to Ge by electron irradiation.

Peaks between 30 and 40 eV are the Ge M_{45} edge. It is noted that the fine structures of the Ge M_{34} edge also changes with the increase of irradiation. The changes can be clearly seen in the derivative of spectrum in Fig. 3. The onset of the M_{45} edge is at about 32.0 eV in the initial spectrum, while it shifts to about 30.3 eV after 3 min of irradiation. Interestingly, there is a step at about 28 eV in the initial spectrum (indicated by a white arrow). The electronic structure calculations in crystalline GeO_2 indicate that only O 2*s* states appear about 28 eV below the lowest unoccupied states. (Results are not shown here.) Therefore we can assign this step to the interband transitions from O 2*s* to the unoccupied states. It disappears after 3 min of irradiation. This implies that oxygen disappears from the irradiated region. The loss of O is also proven by the absence of O *K* edge after several minutes of irradiation.

The background subtracted EELS spectra of the Ge M_{45} edge are shown in Fig. 4. The threshold shift of the core-loss edge is the characteristic of valence state transition. In ox-

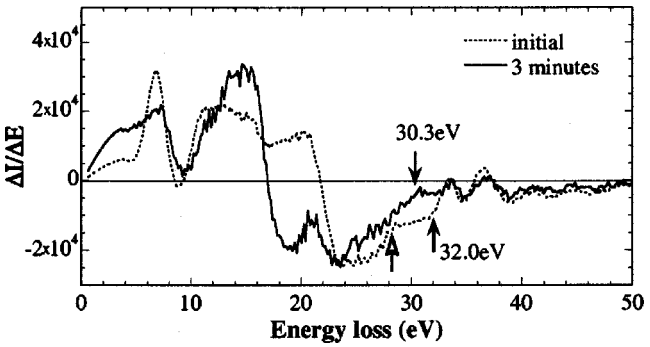

FIG. 3. Derivative of EELS spectrum.

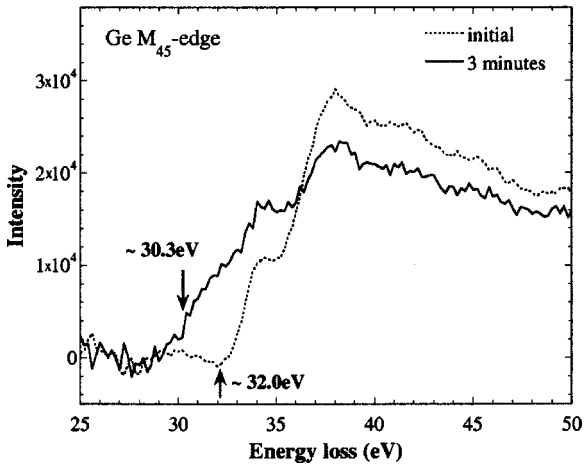

FIG. 4. Background subtracted EELS spectrum of the Ge M_{45} edge.

ides, the charge density of valence electrons around Ge is less than that in the metallic Ge, due to the transfer of the valence charge of Ge to O. Combining with the evidence of bulk plasmon shift (Fig. 2), the shift of the Ge M_{45} edge, by about 1.7 eV, clearly indicates that the GeO_2 within illuminated region has been reduced into Ge completely within only 3 min. To summarize, we suggest that the dark contrasts formed by electron irradiation in Fig. 1(b) are Ge (or at least Ge-rich) nanoparticles.

According to this and the previous works on GeO_2-SiO_2, it clearly shows that Ge and Ge-rich nanoparticles can be formed extremely easily in both conventional TEM and STEM without special modification to the instruments. We have known that electron irradiation has a tendency to eliminate *M*–O–Si (*M* represents cation) configuration in silicate glasses, and decompose the glass phase into cation rich and poor regions.[16,17] The mechanism of beam damage in GeO_2-SiO_2 glasses is probably also related to such a tendency. In GeO_2 glass, however, the mechanism may be different from that in silicate glasses. Recently, we observed crystallization of Te–W alloys in WO_3-TeO_2 glasses by electron irradiation.[18] The mechanism involving the nucleation and growth process on surfaces has been revealed by *in situ* EELS study. Formation of Ge nanoparticles in GeO_2 glasses may also have the same process. Two evidences support this argument. One is that no O_2 signal has been detected by the *in situ* EELS of O *K* edge during the irradiation, and the other is that both Ge and GeO_2 coexist during the reduction of GeO_2 according to the bulk plasmon peaks. Additionally, the smooth of the edge [Fig. 1(b)] also suggests significant surface diffusion. We believe that Bi_2O_3 should not play an important role in this, simply because of its low concentration.

In conclusion, both GeO_2 and GeO_2-SiO_2 glasses are extremely sensitive to high energy electrons. Ge nanoparticles can be precipitated in GeO_2 glasses efficiently by high-energy electron irradiation. Therefore it is necessary that extreme caution should be exercised when the TEM observations are carried out in identifying nanostructures in irradiation sensitive materials.

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